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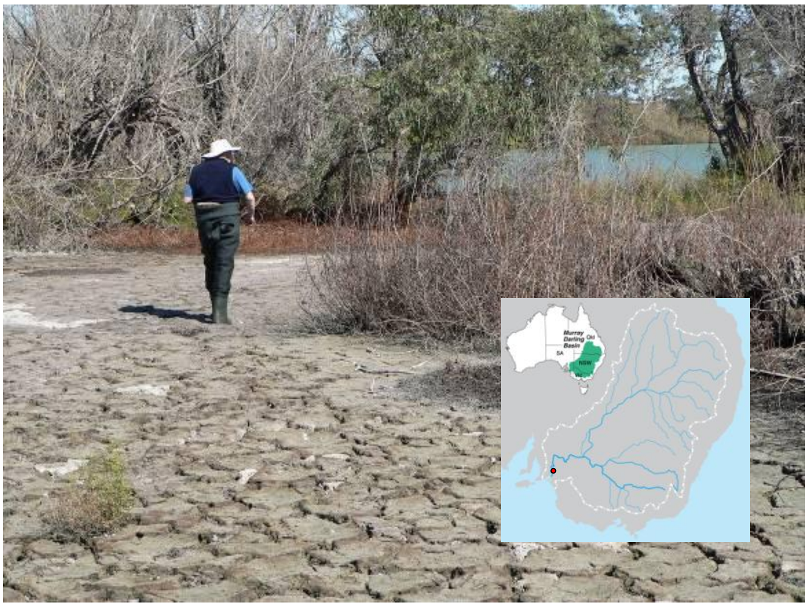

# Assessment of Acid Sulfate Soil Materials (Phase 2) Swanport wetland, South Australia

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

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**Cover Photograph:**

Swanport wetland
Photographer: Rob Fitzpatrick
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# EXECUTIVE SUMMARY

An initial Phase 1 acid sulfate soil investigation of the Swanport wetland in August 2007 (WL samples) and January 2008 (SPM samples) 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 Swanport 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 all metals and metalloids studied. Although the concentrations did not breach sediment quality guidelines and soil ecological investigation level trigger values, the concentrations of many elements were high enough that they may impact water quality if mobilised, particularly for aluminium (Al) and iron (Fe).

The **contaminant and metalloid dynamics** tests were undertaken to assess the release of metals during a water extraction, and to assess dynamics in response to saturation over time by incubating soil materials for periods of 1, 7, 14 and 35 days. The degree to which metal and metalloid concentrations exceed guideline values (ANZECC/ARMCANZ 2000) was used to characterise the degree of hazard. For Swanport wetland, aluminium (Al) and iron (Fe) were assigned a high hazard with concentrations exceeding ANZECC/ARMCANZ environmental protection guidelines by more than 100 times, and cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni) 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 remained very acidic in all samples throughout the tests. Over the duration of the analysis, there was a slight decrease in Eh, which is thought to be responsible for increasing iron (Fe) solubility over time. The release of iron (Fe) coincided with increases in arsenic (As), vanadium (V) and chromium (Cr), these metals probably coming from the dissolution of iron (Fe)-bearing minerals. Cobalt (Co) and nickel (Ni) were more closely associated with manganese.

The Swanport wetland has been classified as medium conservation status by the SA Murray-Darling Basin Natural Resources Management Board (Miles *et al*. 2010). The main hazards considered in this study that may impact on wetland values are acidification, contaminant mobilisation and deoxygenation. The wetland has been allocated a **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 a **medium** (minor consequence) to **very high** (major consequence) **risk** rating due to both **acidification** and **contaminant mobilisation**. The risk associated with **deoxygenation** was determined to be **low** as there was no identified hazard associated with monosulfide formation and no evidence of monosulfides either in the wetland at the time of the Phase 1 field survey or forming during laboratory experiments.

In designing a management strategy for dealing with acid sulfate soils in Swanport wetland, other values and uses of the wetland need to be taken into account to ensure that any intervention is compatible with other management plans and objectives for the wetland.

The wetland soils studied were largely dry at the time of sampling, therefore management options considered should relate to controlling or treating acidification and the protection of connected or adjacent wetlands. Due to the medium to very high risks to the wetland values associated with acidification and contaminant mobilisation in Swanport 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).

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

Swanport wetland 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. The Phase 1 assessment identified 2 high priority sites based on the presence of sulfuric materials and 4 high priority sites based on the presence of sulfidic materials. Phase 2 investigations were carried out on selected surface soil samples from high priority sites identified in the Phase 1 assessment.

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

| Priority | Soil material |
|---|---|
| **High Priority** | All sulfuric materials.<br>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).<br>All hyposulfidic materials with $S_{CR}$ contents ≥ 0.10% S.<br>All surface soil materials (i.e. within 0-20 cm) with water soluble sulfate (1:5 soil:water) contents ≥100 mg $kg^{-1}$ $SO_4$.<br>All monosulfidic materials. |
| **Moderate Priority** | All hyposulfidic materials with $S_{CR}$ contents < 0.10% S. |
| **No Further Assessment** | Other acidic soil materials.<br>All other soil materials. |

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

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

**Table 1-3 Summary of Swanport wetland samples analysed for Phase 2 assessment.**

| Soil Laboratory Test | Swanport wetland samples | Sample depth (cm) | Number of samples analysed |
|---|---|---|---|
| Reactive metals | SPM 1.2 | 0-5 | 4 |
| | SPM 1.3 | 5-10 | |
| | WL 5.4 | 1-5 | |
| | WL 5.5 | 5-20 | |
| Contaminant and metalloid dynamics | SPM 1.2 | 0-5 | 4 |
| | SPM 1.3 | 5-10 | |
| | WL 5.4 | 1-5 | |
| | WL 5.5 | 5-20 | |
| Monosulfide formation potential | SPM 1.2 | 0-5 | 1 |
| Mineral identification by X-ray diffraction (XRD) | SPM 1.1 | 0-0.02 | 4 |
| | WL 5.1 | 0-0.02 | |
| | WL 5.2 | 0-0.02 | |
| | WL 5.3 | 0-1 | |

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

# 2. LABORATORY METHODS

## 2.1. Laboratory analysis methods

### 2.1.1. Summary of laboratory methods

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

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

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

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

### 2.1.2. Reactive metals method

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

### 2.1.3. Contaminant and metalloid dynamics method

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

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

### 2.1.4. Monosulfide formation potential method

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

The reactive iron (Fe) fraction in field moist sediments was extracted using 1.0 M HCl (Claff *et al.* 2010). The ferrous iron ($Fe^{2+}$) and total iron ($Fe^{2+}$ + $Fe^{3+}$) fractions were immediately fixed following extraction. The ferrous iron trap was made up from a phenanthroline solution with an ammonium acetate buffer (APHA 2005), and the total iron trap also included a hydroxylamine solution (APHA 2005). The iron species were quantified colorimetrically using a Hach DR 2800 spectrophotometer.

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

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

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

## 2.2. Quality assurance and quality control

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

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

# 3. RESULTS AND DISCUSSION

## 3.1. Summary of soil laboratory results

### 3.1.1. Reactive metals data

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

The concentrations of metals and metalloids were below sediment quality guideline (SQG) values and soil ecological investigation levels (EIL) for those elements for which guidelines exist. The concentrations for most reactive metals and metalloids are relatively low, but relatively high for aluminium (Al) and iron (Fe) (Table 3-1).

**Table 3-1 Swanport wetland reactive metals data.**

Concentrations in mg kg$^{-1}$ and µg kg$^{-1}$ as indicated.

| Sample | Ag* | Al | As | Cd* | Co | Cr* | Cu | Fe | Mn | Ni | Pb | Sb* | Se* | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SPM 1.2 | 6.1 | 531 | 1.5 | 32 | 5.1 | 200 | 7.1 | 1128 | 44 | 8.9 | 0.59 | < 10 | 45 | 7.1 | 6.2 |
| SPM 1.3 | 8.8 | 495 | 1.2 | 22 | 2.0 | 147 | 5.6 | 1019 | 26 | 6.6 | 3.5 | <15 | 51 | 6.5 | 1.8 |
| WL 5.4 | 6.9 | 276 | 0.68 | 9.8 | 1.2 | 285 | 4.2 | 3180 | 12 | 3.3 | 0.87 | < 22 | 36 | 4.2 | 2.1 |
| WL 5.5 | 10 | 729 | 1.2 | 44 | 2.8 | 309 | 5.0 | 1812 | 26 | 6.8 | 4.4 | < 19 | 61 | 7.3 | 4.3 |
| | | | | | | | | | | | | | | | |
| [1]SQG | 1000 | - | 20 | 1500 | - | 80000 | 65 | - | - | 21 | 50 | 2000 | - | - | 200 |
| [2]Soil EIL | - | - | 20 | 3000 | - | - | 100 | - | 500 | 60 | 600 | - | - | 50 | 200 |

* Units are in µg kg$^{-1}$

< value is below detection limit

[1] SQG: Sediment Quality Guideline Value (Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000)

[2] Soil EIL: Soil – Ecological Investigation Level (NEPC 1999)

### 3.1.2. Contaminant and metalloid dynamics data

The contaminant and metalloid dynamics data for the four Swanport 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 | Swanport | | |
|---|---|---|---|---|---|
| | | | **Min.** | **Median** | **Max.** |
| pH | | 6.5-8.0 | **3.1** | **3.5** | **5.2** |
| EC* | $\mu S\ cm^{-1}$ | 2200 | 292 | 672 | 1495 |
| Eh | mV | - | 61.5 | 611.5 | 724 |
| Ag | $\mu g\ l^{-1}$ | 0.05 | <0.01 | <0.1 | <0.1 |
| $Al^{A}$ | $mg\ l^{-1}$ | 0.055 | **0.35** | **1.4** | **8.0** |
| $As^{B}$ | $\mu g\ l^{-1}$ | 13 | <0.5 | 1.4 | **56** |
| Cd | $\mu g\ l^{-1}$ | 0.2 | <0.2 | **0.30** | **0.91** |
| Co | $\mu g\ l^{-1}$ | 2.8 | **17** | **48** | **168** |
| $Cr^{C}$ | $\mu g\ l^{-1}$ | 1 | 0.84 | **1.8** | **15** |
| $Cu^{H}$ | $\mu g\ l^{-1}$ | 1.4 | <2 | **10** | **18** |
| $Fe^{I}$ | $mg\ l^{-1}$ | 0.3 | 0.16 | **5.0** | **186** |
| Mn | $\mu g\ l^{-1}$ | 1700 | 211 | 625 | **2133** |
| $Ni^{H}$ | $\mu g\ l^{-1}$ | 11 | **28** | **88** | **228** |
| $Pb^{H}$ | $\mu g\ l^{-1}$ | 3.4 | <1 | <2 | **4.4** |
| Sb | $\mu g\ l^{-1}$ | 9 | <2 | <10 | <10 |
| Se | $\mu g\ l^{-1}$ | 11 | <0.14 | 0.20 | 1.2 |
| V | $\mu g\ l^{-1}$ | 6 | <0.5 | 2.1 | **39** |
| $Zn^{H}$ | $\mu g\ l^{-1}$ | 8 | <3 | **50** | **186** |

🟨 ***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 $\mu S\ cm^{-1}$) for freshwater lowland rivers in South-east Australia is provided for salinity (there are currently no trigger values defined for 'Wetlands'.)*

$^{A}$ *Guideline is for Aluminium in freshwater where pH > 6.5.*
$^{B}$ *Guideline assumes As in solution as Arsenic (AsV).*
$^{C}$ *Guideline for Chromium is applicable to Chromium (CrVI) only.*
$^{H}$ *Hardness affected (refer to Guidelines).*
$^{I}$ *Fe Guideline for recreational purposes.*

The pH of the soil materials remained below the lower ANZECC/ARMCANZ environmental protection guideline of pH 6.5 and showed little change over the 35 day incubation period (Figure 3-1), although there was a slight increase in sample SPM 1.2 by day 35 of the incubation. The pH for three of the four soil samples analysed (from both profiles) remained sulfuric implying significant acid buffering in the Swanport wetland soils.

The Eh was initially very high, but started to show a slight decrease by day 35 in three of the samples (Figure 3-1). The surface soil SPM 1.2 showed a more significant decrease to moderately reducing conditions. The SEC remained relatively constant up to day 14, thereafter decreasing (Figure 3-1).

Manganese concentrations were moderately high throughout the contaminant and metalloid dynamics tests, but were only above ANZECC/ARMCANZ environmental protection guideline values in SPM 1.2 for the 24 hour sample (Figure 3-2). Iron (Fe) concentrations showed a consistent increase over time for all samples, and concentrations were up to more than 600 times the ANZECC/ARMCANZ environmental protection guideline.

Most trace elements were above the ANZECC/ARMCANZ environmental protection guidelines (Table 3-2) and were released rapidly as evidenced by day 1 contaminant and metalloid dynamics analyses. Aluminium (Al) concentrations were very high as expected for the low pH, particularly in sample SPM 1.2, and all samples showed a slight decrease over time following rapid release after 24 hours (Figure 3-1). The surface sample SPM 1.2 had the highest concentrations for a number of metals including aluminium (Al), arsenic (As), cobalt (Co), chromium (Cr), iron (Fe), manganese (Mn), nickel (Ni), vanadium (V) and zinc (Zn). The concentrations were largely controlled by pH which is a major control on metal solubility, but appear to be strongly modified by the dissolution of iron (Fe) and manganese (Mn)-bearing minerals. Arsenic (As), vanadium (V) and chromium (Cr) showed a strong tendency to increase in concentration over time (Figure 3-1 and Figure 3-3), possibly controlled by release from an iron-bearing mineral (oxyhydroxide or oxyhydroxysulfate), although both elements decreased in sample SPM 1.2 by day 35. Cobalt (Co), nickel (Ni) and cadmium (Cd) displayed similar trends to manganese (Mn), which may control their mobility in the Swanport wetland soils.

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 little trend with pH (Figure 3-4), but arsenic (As), vanadium (V) and chromium (Cr) were similar to iron (Fe), correlating with pH. The changes in concentration of iron (Fe) over the time period are largely attributed to a decrease in Eh, allowing iron to increase by reductive dissolution of an iron-bearing mineral (iron hydroxysulfate or hydroxide phase). The low concentrations of iron, manganese and other trace metals and metalloids at low pH (Figure 3-3) may be due to the stability of a iron-hydroxysulfate at low pH as these were noted as surface mineral efflorescences in this wetland (Fitzpatrick *et al*. 2010).

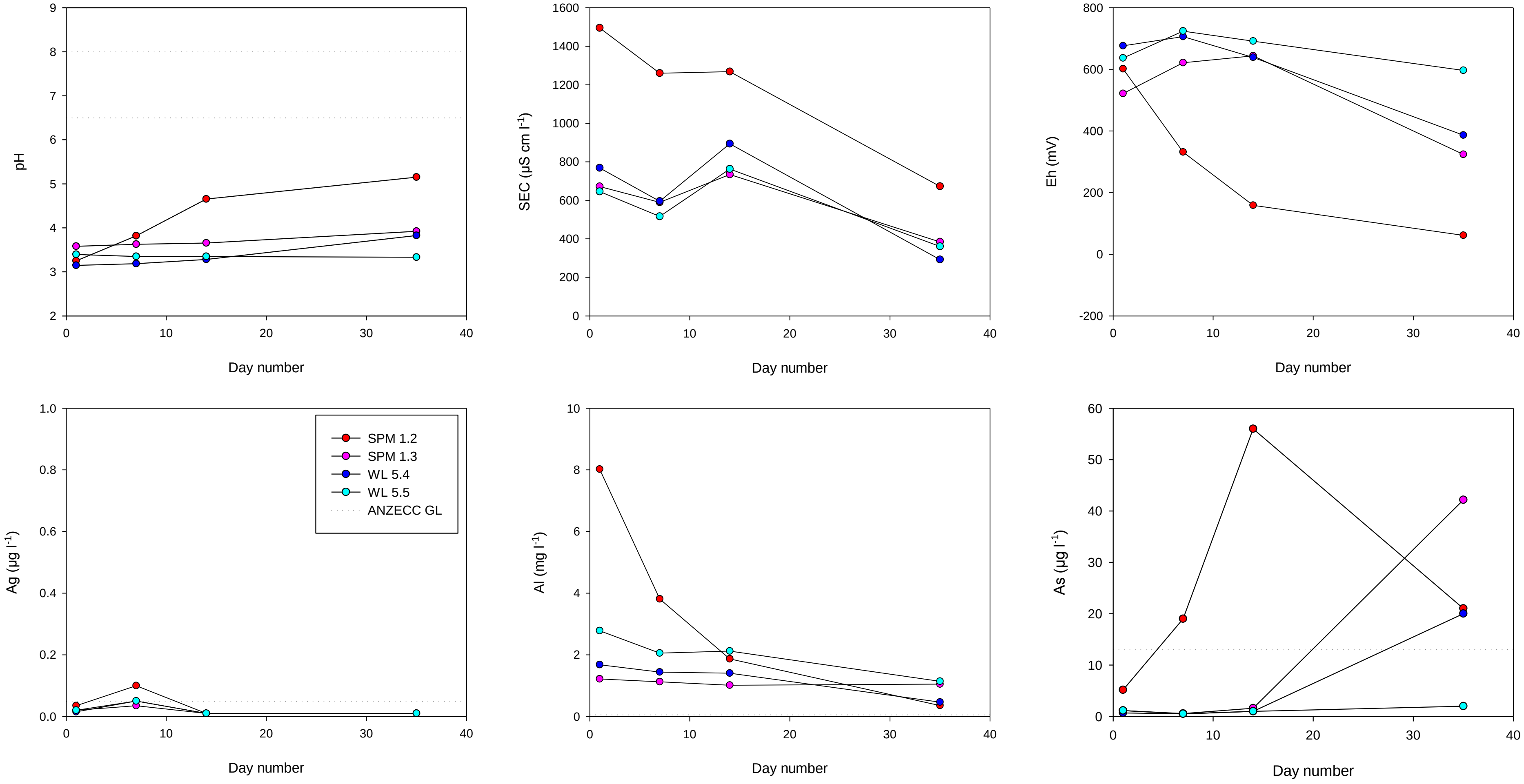

**Figure 3-1 Contaminant and metalloid dynamics results for Swanport wetland soil materials for pH, SEC, Eh, silver (Ag), aluminium (Al) and arsenic (As).**

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

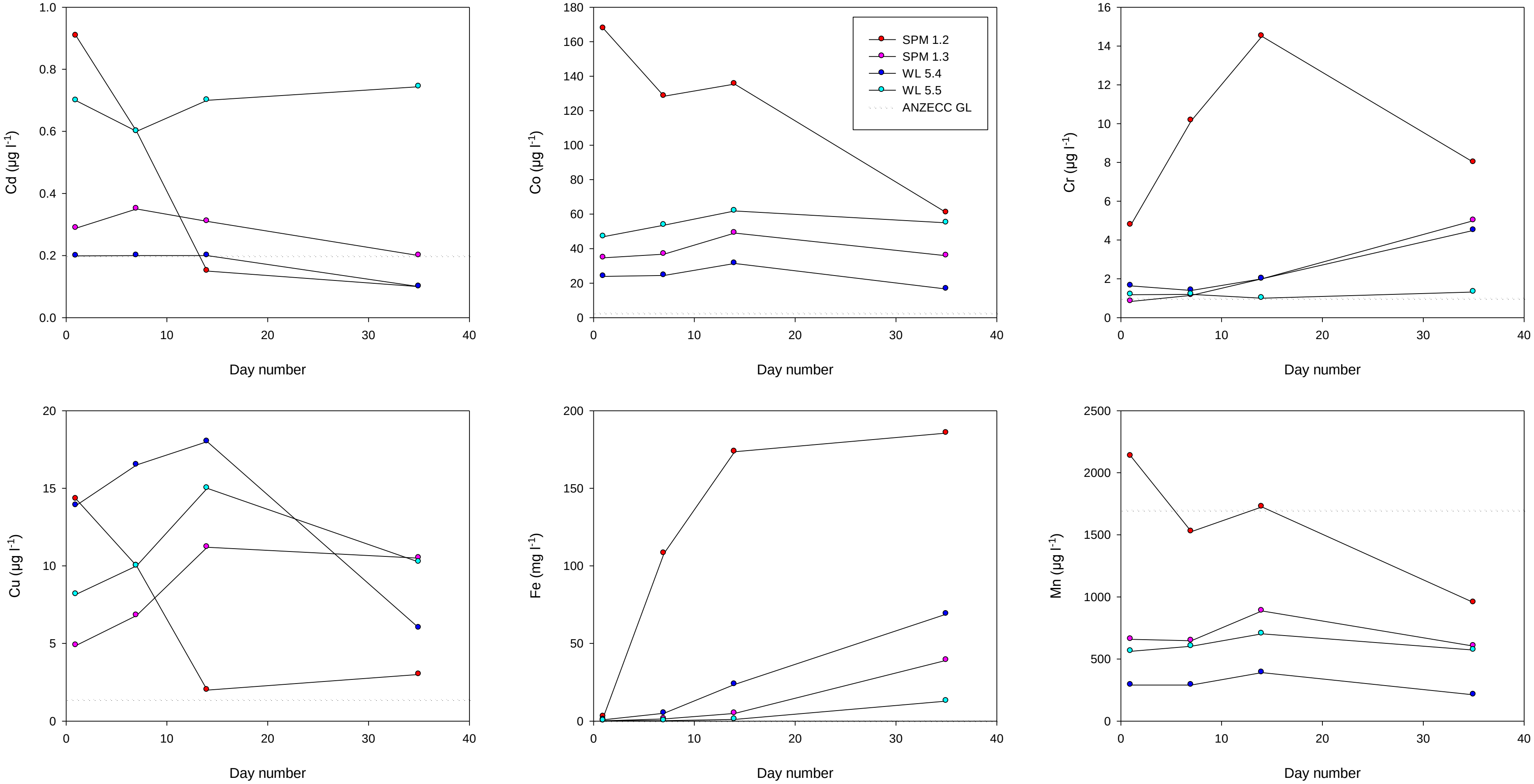

**Figure 3-2 Contaminant and metalloid dynamics results for Swanport wetland soil materials for cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe) and manganese (Mn).**

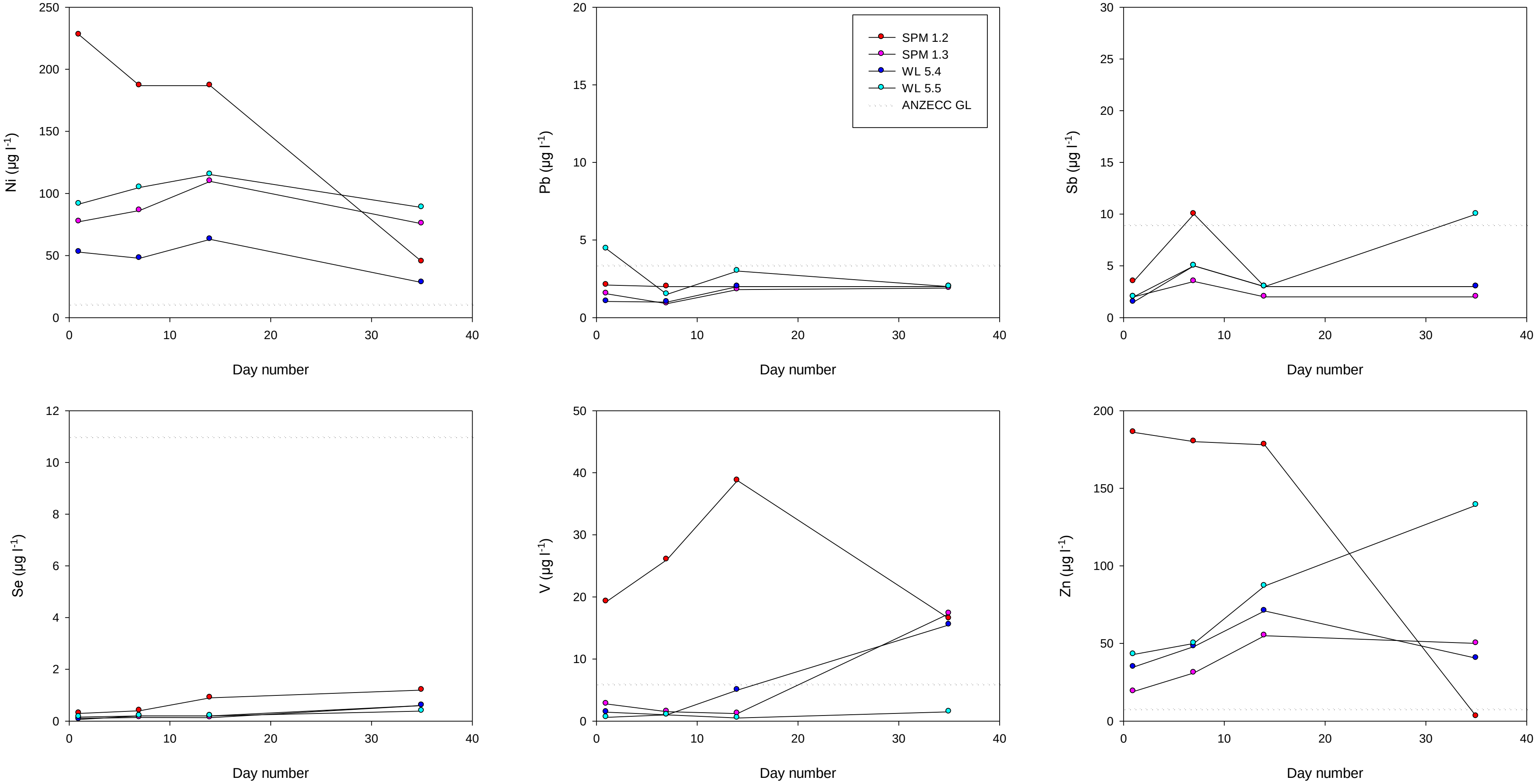

**Figure 3-3 Contaminant and metalloid dynamics results for Swanport wetland soil materials for nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn).**

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

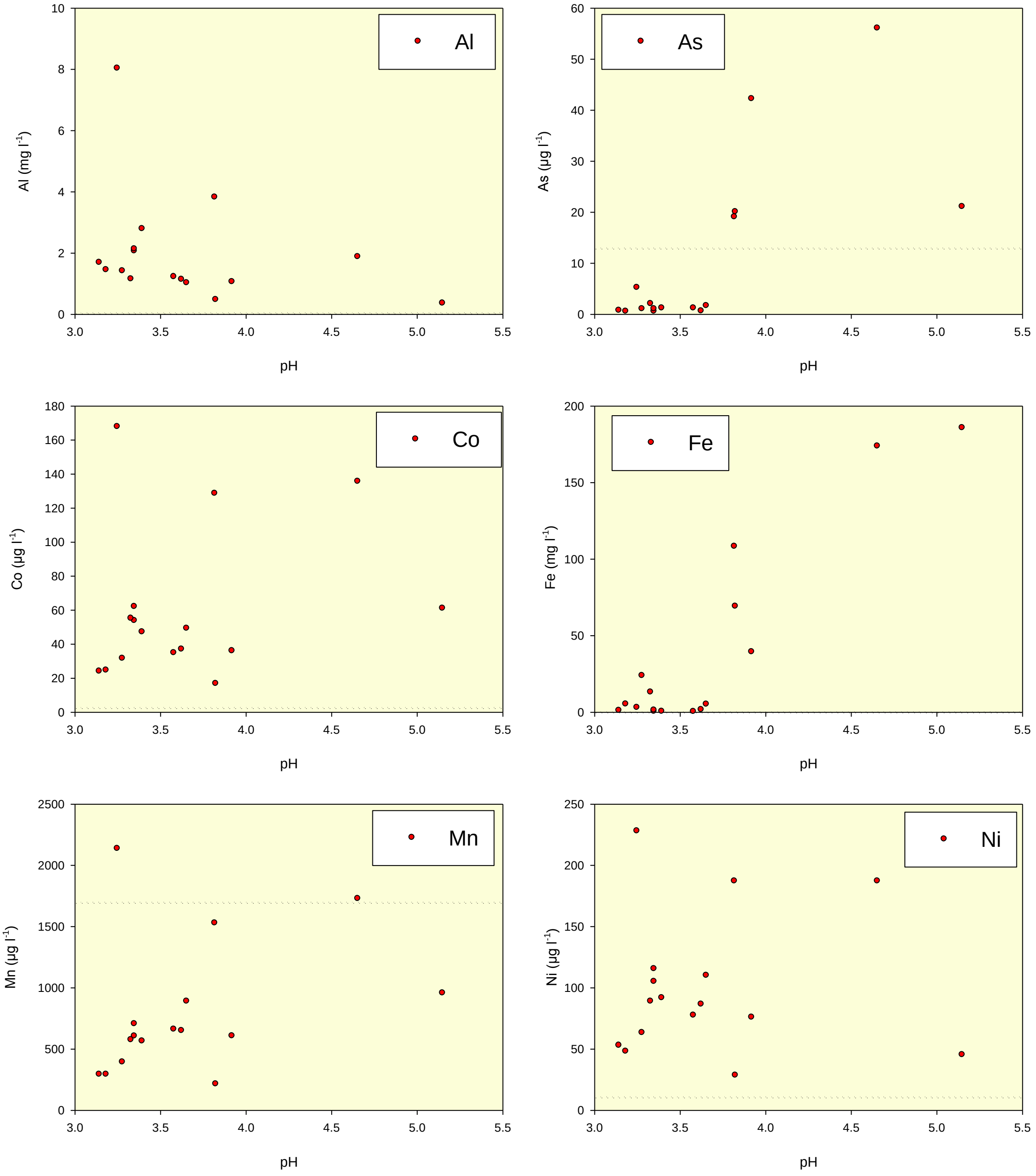

**Figure 3-4 Selected trace elements plotted against pH.**

## 3.1.3. Monosulfide formation potential data

The monosulfide formation potential data for the sample analysed from Swanport wetland (SPM 1.2) are shown in Table 3-3. The pH of the soil water changed from 3.56 to 4.09 over the seven week incubation period. The pH increase was slightly less than that from the contaminant and metalloid dynamics tests, where pH reached 5.15 (Figure 3-1).

The Eh decreased significantly from 538 to 159 mV indicating a significant change to more reducing conditions (Table 3-5). The Eh data are generally consistent with the contaminant and metalloid dynamics experiments where Eh decreased from 601 to 61 mV (Figure 3-1).

**Table 3-3 Summary of monosulfide formation potential data for the Swanport wetland surface soil materials after 7 weeks (3.6 g/L sucrose).**

| Inundation Time | Parameter | Units | SPM 1.2 |
|---|---|---|---|
| Day 0 | Total Fe | mg/kg | 9158 |
| | Fe(II)$^-$ | mg/kg | 2277 |
| | Sulfate* | mg/kg | 2226 |
| | pH | | 3.56 |
| | Eh | mV | 538 |
| Week 7 | pH | | 4.09 |
| | Eh | mV | 159 |
| | $S_{AV}$ | Wt. %S | <0.01 |
| | $S^o$ | Wt. %S | <0.01 |
| | Pyrite-S | Wt. %S | 0.03 |
| | Dissolved $S^{2-}$ | µg/L | 466 |

*completed during Phase 1

After 7 weeks, acid volatile sulfide ($S_{AV}$) and elemental sulfur ($S^0$) were both <0.01% and pyrite-S was present at 0.03% (Table 3-3). It appears, therefore, that monosulfide formation has not occurred in this sample during the tests. The sample originally contained 0.08 % $S_{CR}$ ($S_{AV}$ + pyrite-S) and it, therefore, appears that pyrite has not formed in the sample during the experiment. Dissolved sulfide was present (466 µg/L, Table 3-3), suggesting that conditions are sufficiently reducing for pyrite to form, but at the low pH maintained by week 7 (4.09, Table 3-3), it is likely that reaction kinetics are very slow.

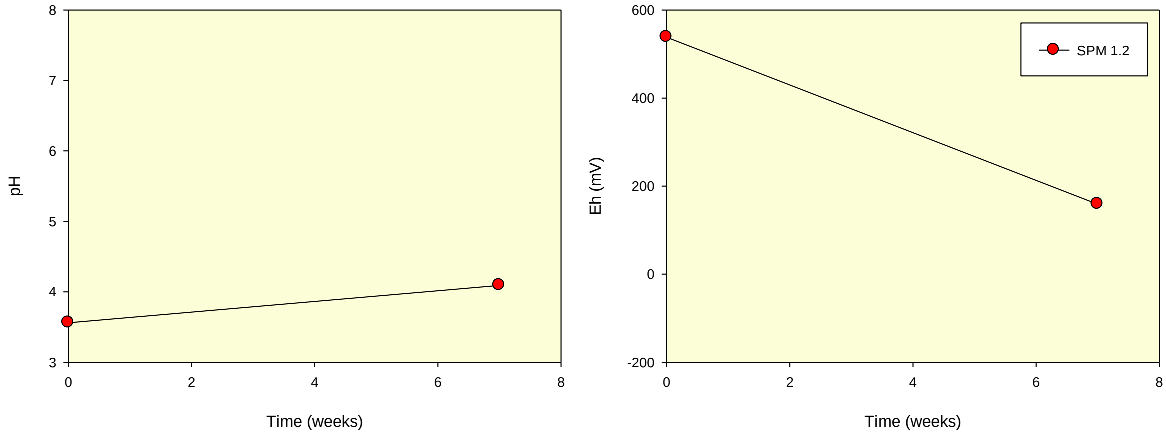

**Figure 3-5 pH and Eh dynamics during monosulfide formation potential tests in surface soil sample SPM 1.2 from Swanport wetland.**

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

Four surface mineral efflorescences were sampled from the profiles in the Swanport wetland: SPM 1.1, WL 5.1, WL 5.2 and WL 5.3 corresponding to the profiles studied for reactive metals and contaminant and metalloid dynamics tests. The mineralogy is shown on Table 3-4, and photographs and XRD patterns provided in Appendix 4. The mineral efflorescences noted in SPM 1 profile are jarosite ($KFe_3(SO_4)_2(OH)_6$), natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) and minor gypsum ($CaSO_4.2H_2O$). In profile WL 5, the additional rare minerals hexahydrite ($MgSO_4.6H_2O$), metavoltine ($K_2Na_6Fe^{2+}Fe^{3+}_6(SO_4)12O_2.18H_2O$) and pickeringite ($MgAl_2(SO_4)_4.22H_2O$) were also identified. The salts gypsum and hexahydrite 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 mineral metavoltine is stable at lower pH than natrojarosite and jarosite and found on the edges of peds where evaporation during drying led to extremely low pH (Figure 3-6).

**Table 3-4 Summary of X-ray diffraction results**

| Sample number | Depth (cm) | Mineralogy |
|---|---|---|
| SPM1.1 | 0-0.02 | Dominant quartz, sub-dominant jarosite and natrojarosite, minor gypsum, trace albite, orthoclase and mica |
| WL5.1 | 0-0.02 | Dominant quartz, minor gypsum, hexahydrite, metavoltine and pickeringite |
| WL5.2 | 0-0.02 | Co-dominant quartz and gypsum, sub-dominant jarosite and/or natrojarosite, trace mica, orthoclase and hexahydrite |
| WL5.3 | 0-1 | Co-dominant quartz and gypsum, sub-dominant jarosite and/or natrojarosite, trace mica, orthoclase, kaolin and hexahydrite |

It is likely that the acid-generating aluminium (Al) and iron-hydroxysulfate salts also store metals and metalloids which get released during dissolution of these minerals following rewetting.

**Figure 3-6 Bright yellow metavoltine (right) forming at the edge of a ped near profile WL 5 (left).**

## 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 $kg^{-1}$) compared to water quality guidelines (generally µg $kg^{-1}$) that significant release could pose a hazard to soil and surface water quality.

The **contaminant and metalloid dynamics** 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.

It would appear that reductive processes have begun in the samples analysed with a slight decrease in Eh for most samples by day 35. The largest decrease in Eh was in surface sample SPM 1.2 (Figure 3-1), which also displayed the largest increase in pH. The pH in the other samples remained less than pH 4 and this may well hinder bacterially mediated reduction reactions. The maintenance of low pH of the samples implies significant pH buffering by soil minerals and dissolved species, consistent with the abundance of acid-generating mineral efflorescences. For a number of elements, the highest concentrations were present in day 1 samples, showing rapid release from soil minerals. The main exceptions were iron (Fe) which increased over time, and those elements which commonly form negatively charged oxyanions such as arsenic (As), vanadium (V) and chromium (Cr). It is considered likely that the dissolution of iron-bearing minerals (most likely hydroxysulfates) controls the abundances of these oxyanions. In contrast, the metals cobalt (Co), nickel (Ni) and possibly zinc (Zn) display a more similar trend to manganese (Mn), which may control their release to solution. The pH of the solutions, however, is such that many metals have remained in solution at moderately high concentration. The behaviour of the metals and metalloids is, therefore, not simple, and appears to be a complex interplay of both pH and Eh changes and the stability of different iron (Fe)- and manganese (Mn)-bearing minerals.

A number of trace metals are very high, being greater than 100x ANZECC/ARMCANZ environmental protection guideline values (Table 3-2). The degree to which samples exceed guideline concentrations has been used to assign a degree of hazard (Table 3-5). For some samples which required dilution, the detection limits were slightly above ANZECC/ARMCANZ environmental protection guideline values due to required dilution. The detection limit for silver (Ag), for example, was up to 0.1 µg $l^{-1}$ (ANZECC guideline 0.05 µg $l^{-1}$). Antimony (Sb) was below detection limit for all samples (detection limit varying between 2 and 10 µg $l^{-1}$). It is therefore not possible to group these in Table 3-5, although it can be concluded that they present either a low hazard or no hazard. The data are shown in Appendix 1 which displays the detection limits for individual analyses.

Of particular significance for Swanport wetland are the high hazards for aluminium (Al) and iron (Fe), and moderate hazards for cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni) and zinc (Zn) (Table 3-5). This is especially so as pH showed little increase and concentrations of metals remained high over the duration of the 35 days. The data are consistent with the high net acidities noted by Fitzpatrick *et al*. (2010), which varied from -24 up to 352 mol $H^+$/tonne (median of 315 mol $H^+$/tonne), which may mean that the soils will take a significant time to recover from acidification. The samples were reanalysed in this study as retained acidity was not completed in the earlier work. Net acidity for the samples studied varied from 254 to 379 mol $H^+$/tonne, slightly higher than phase 1. These high net acidities are likely to buffer the pH to low values until acidity is neutralised or consumed and mean that an increase in soil pH is likely to be initially slow.

**Table 3-5 Summary of the degree of hazard associated with the measured contaminant and metalloid concentrations in the Swanport 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, Mn, Pb, V |
| Moderate Hazard | Value exceeds ANZECC/ARMCANZ guideline threshold by 10x or more, but is less than 100x exceedance | Co, Cr, Cu, Ni, Zn |
| High Hazard | Value exceeds ANZECC/ARMCANZ guideline threshold by 100x or more | Al, Fe |

Note: Ag and Sb were below detection limits due to dilutions, and therefore are likely to be in the low or no hazard classification.

The **monosulfide formation potential** test assists in determining the propensity for monosulfides to form during future inundation. The sample used for this test contained no acid volatile sulfide ($S_{AV}$), and elemental sulfur ($S^0$) was very close to the detection limit, with reduced sulfur being dominated by pyrite-S. The lack of acid volatile sulfide ($S_{AV}$) ranks the monosulfide formation potential hazard as ‘No hazard’ (Table 3-6).

**Table 3-6 Guideline thresholds for the degree of hazard associated with acid volatile sulfide ($S_{AV}$) concentrations.**

| Degree of Hazard | Guideline Threshold |
|---|---|
| No Hazard | < 0.01 % $S_{AV}$ |
| Low Hazard | 0.01 % $S_{AV}$ |
| Moderate Hazard | >0.01-0.05 % $S_{AV}$ |
| High Hazard | > 0.05 % $S_{AV}$ |

# 4. RISK ASSESSMENT

## 4.1. Risk assessment framework

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

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

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

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

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

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

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

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

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

| Likelihood category | Consequences category | | | | |
|---|---|---|---|---|---|
| | Extreme | Major | Moderate | Minor | Insignificant |
| Almost certain | Very High | Very High | High | Medium | Low |
| Likely | Very High | High | Medium | Medium | Low |
| Possible | High | High | Medium | Low | Low |
| Unlikely | High | Medium | Medium | Low | Very low |
| Rare | High | Medium | Low | Very low | Very low |

It is suggested that:

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

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

## 4.2. Assessment of risks

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

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

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

### 4.2.1. Risks associated with acidification

The high net acidities in samples from Swanport wetland show that the acidification hazard is high. Net acidities were very high in the upper layers of the soils where oxidation had taken place and the presence of mineral efflorescences suggests an upward movement of acidity and possibly metals. Both titratable actual acidity (TAA) and retained acidity were high in these shallow soil layers, and relatively low $S_{CR}$ was present in the deeper unoxidised materials giving rise to much lower net acidity.

The probability of soil acidification is considered high as evidenced by the sulfuric nature of the soils (pH down to pH 2.5). 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 clayey soils in this wetland, it is unlikely that soil acidification will be mediated by high flows. The consequences are likely to be significant for soil ecology, but the timescale for soil recovery from acidification cannot be assessed with existing information. Studies in other wetlands e.g. Nelwart Lagoon (Shand *et al.* 2010) indicate that in areas with strongly acidic soils such as Swanport wetland, 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 (major consequence). 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 (minor consequence). The *risk to 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 by mineral breakdown, they are likely to be mobile, especially if pH is low. Although reduction processes may lead to reincorporation of metals and metalloids into sulfide minerals (following sulfate reduction), at intermediate redox potentials mobility may be high where iron (Fe) and manganese (Mn) are soluble. The reactive metals and contaminant and metalloid dynamics results attest to the availability and mobility of a number of metals, particularly aluminium (Al), iron (Fe), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni) 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.* 2011), 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 Swanport 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 (major consequence). 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 (minor consequence). The risk rating is therefore likely to vary from **medium** to **very high** depending on future scenarios.

### 4.2.3. Risks associated with de-oxygenation

Monosulfidic materials are considered the main cause of deoxygenation risk in acid sulfate soils. The water soluble sulfate concentrations in the sample were high and above the trigger value for monosulfidic black ooze formation (MDBA 2010).

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 Summary of risks associated with acid sulfate soil materials in Swanport wetland.**

| Acidification Risk | | Contaminant mobilisation | | Deoxygenation |
|---|---|---|---|---|
| *Soil* | *Water* | *Soil* | *Water* | |
| Very high | Medium-very high | Very high | Medium-very high | Low |

# 5. BROAD ACID SULFATE SOIL MANAGEMENT OPTIONS

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

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

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

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

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

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

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

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

| Management Objective | Activities |
|---|---|
| **1. Minimising the formation of acid sulfate soils in inland aquatic ecosystems** | **Reduce secondary salinisation through:**<br>• Lowering saline water tables<br>• Maintaining the freshwater lens between saline groundwater and the aquatic ecosystem<br>• Stopping the delivery of irrigation return water<br>• Incorporating a more natural flow regime. |
| **2. Preventing oxidation of acid sulfate soils or controlled oxidation to remove acid sulfate soils** | **Preventing oxidation:**<br>• Keep the sediments covered by water<br>• Avoid flow regimes that could re-suspend sediments.<br>**Controlled oxidation:**<br>• Assess whether neutralising capacity of the sediments and water far exceeds the acidity produced by oxidation<br>• Assess the risk of deoxygenation and metal release. Monitor intervention and have a contingency plan to ensure avoidance of these risks. |
| **3. Controlling or treating acidification** | • Neutralise water column and/or sediments by adding chemical ameliorants<br>• Add organic matter to promote bioremediation by micro-organisms<br>• Use stored alkalinity in the ecosystem. |
| **4. Protecting adjacent or downstream environments if treatment of the affected aquatic ecosystem is not feasible** | • Isolate the site<br>• Neutralise and dilute surface water<br>• Treat discharge waters by neutralisation or biological treatment. |
| **5. Limited further intervention** | • Assess risk<br>• Communicate with stakeholders<br>• Undertake monitoring<br>• Assess responsibilities and obligations and take action as required. |

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# APPENDICES

# APPENDIX 1 REACTIVE METALS DATA

## Swanport wetland

| Sample | Depth | Analysis | Ag* | Al | As | Cd* | Co | Cr* | Cu | Fe | Mn | Ni | Pb | Sb* | Se* | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SPM 1.2 | 0-5 | a | 6.3 | 530 | 1.5 | 32 | 5.2 | 203 | 7.0 | 1131 | 44 | 8.8 | 0.56 | < 10 | 45 | 7.1 | 6.1 |
| | | b | 5.9 | 532 | 1.5 | 32 | 5.0 | 196 | 7.1 | 1126 | 43 | 8.9 | 0.61 | < 10 | 45 | 7.2 | 6.4 |
| SPM 1.3 | 5-10 | a | 8.4 | 472 | 1.1 | 21 | 2.0 | 138 | 5.4 | 958 | 25 | 6.4 | 3.4 | < 15 | 50 | 6.2 | 1.7 |
| | | b | 9.1 | 519 | 1.2 | 22 | 2.1 | 156 | 5.8 | 1079 | 26 | 6.9 | 3.5 | < 15 | 53 | 6.9 | 1.8 |
| WL 5.4 | 1-5 | a | 7.3 | 281 | 0.72 | 10 | 1.3 | 291 | 4.2 | 3286 | 12 | 3.3 | 0.86 | < 22 | 38 | 4.4 | 2.0 |
| | | b | 6.5 | 271 | 0.65 | 9.4 | 1.2 | 280 | 4.1 | 3074 | 12 | 3.3 | 0.87 | < 22 | 34 | 4.1 | 2.1 |
| WL 5.5 | 5-20 | a | 10 | 680 | 1.2 | 40 | 2.6 | 285 | 4.9 | 1671 | 25 | 6.2 | 4.0 | < 19 | 55 | 6.9 | 4.4 |
| | | b | 11 | 777 | 1.3 | 47 | 3.0 | 334 | 5.0 | 1953 | 28 | 7.3 | 4.8 | < 19 | 67 | 7.7 | 4.3 |

Units are mg kg$^{-1}$ unless indicated otherwise as below

* Units are in µg kg$^{-1}$

< value is below detection limit*

# APPENDIX 2 CONTAMINANT AND METALLOID DYNAMICS DATA

Swanport 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 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SPM 1.2 | 1 | 0-5 | a | 604 | 1491 | 3.24 | <0.05 | 7.9 | 5.9 | 0.87 | 168 | 4.4 | 14 | 2.8 | 2131 | 228 | <3 | <5 | 0.31 | 19 | 194 |
| | | | b | 599 | 1498 | 3.26 | <0.02 | 8.2 | 4.5 | 0.94 | 168 | 5.2 | 15 | 2.8 | 2135 | 228 | <1.2 | <2 | 0.29 | 20 | 178 |
| | 7 | | a | 334 | 1241 | 3.85 | <0.1 | 3.8 | 18 | 0.60 | 126 | 11 | 10.0 | 110 | 1497 | 184 | <2 | <10 | 0.40 | 26 | 184 |
| | | | b | 329 | 1279 | 3.79 | <0.1 | 3.9 | 20 | 0.60 | 130 | 9.8 | 10.0 | 106 | 1553 | 190 | <2 | <10 | <0.4 | 26 | 176 |
| | 14 | | a | 164 | 1231 | 4.57 | <0.01 | 1.8 | 50 | 0.10 | 131 | 14 | <2 | 173 | 1660 | 179 | <2 | <3 | 1.0 | 38 | 172 |
| | | | b | 154 | 1305 | 4.74 | <0.01 | 1.9 | 62 | 0.20 | 140 | 15 | <2 | 174 | 1790 | 194 | <2 | <3 | 0.80 | 40 | 184 |
| | 35 | | a | 64 | 670 | 5.10 | <0.01 | 0.32 | 20 | <0.1 | 60 | 8.0 | <3 | 182 | 942 | 46 | <2 | <3 | 1.2 | 16 | <3 |
| | | | b | 59 | 675 | 5.20 | <0.01 | 0.39 | 22 | <0.1 | 62 | 8.0 | <3 | 189 | 965 | 45 | <2 | <3 | 1.2 | 17 | <3 |
| SPM 1.3 | 1 | 5-10 | a | 524 | 611 | 3.57 | <0.02 | 1.3 | 0.92 | 0.23 | 36 | 0.72 | 5.1 | 0.17 | 683 | 81 | 1.6 | <2 | 0.10 | 2.6 | 19 |
| | | | b | 519 | 733 | 3.59 | <0.02 | 1.1 | 1.3 | 0.35 | 33 | 0.95 | 4.6 | 0.16 | 634 | 73 | 1.5 | <2 | 0.11 | 2.9 | 19 |
| | 7 | | a | 584 | 511 | 3.66 | <0.02 | 0.78 | 0.60 | 0.30 | 32 | 1.1 | 5.6 | 0.41 | 575 | 71 | 0.80 | <2 | <0.08 | 2.0 | 24 |
| | | | b | 659 | 668 | 3.59 | <0.05 | 1.5 | <0.5 | 0.40 | 42 | 1.2 | 8.0 | 2.3 | 719 | 102 | <1 | <5 | <0.2 | 1.0 | 38 |
| | 14 | | a | 649 | 691 | 3.66 | <0.01 | 0.85 | 1.2 | 0.32 | 43 | 2.0 | 10 | 3.6 | 813 | 95 | 1.6 | <1 | 0.06 | 1.4 | 48 |
| | | | b | 639 | 778 | 3.65 | <0.01 | 1.2 | 2.0 | 0.30 | 55 | 2.0 | 12 | 6.2 | 960 | 125 | <2 | <3 | <0.2 | 1.0 | 62 |
| | 35 | | a | 259 | 378 | 3.97 | <0.01 | 1.0 | 61 | 0.20 | 34 | 6.0 | 12 | 42 | 584 | 72 | 1.8 | <1 | 0.80 | 24 | 46 |
| | | | b | 389 | 390 | 3.87 | <0.01 | 1.1 | 24 | 0.20 | 37 | 4.0 | 9.0 | 36 | 623 | 79 | <2 | <3 | 0.40 | 11 | 54 |
| WL 5.4 | 1 | 1-5 | a | 674 | 748 | 3.15 | <0.01 | 1.6 | 0.59 | 0.21 | 24 | 1.7 | 14 | 0.85 | 297 | 53 | 1.1 | <1 | 0.06 | 1.4 | 34 |
| | | | b | 679 | 788 | 3.14 | <0.02 | 1.7 | 0.76 | 0.19 | 24 | 1.6 | 13 | 0.93 | 284 | 52 | <1 | <2 | 0.07 | 1.4 | 36 |
| | 7 | | a | 729 | 572 | 3.20 | <0.05 | 1.1 | <0.5 | <0.2 | 22 | 1.2 | 16 | 2.5 | 257 | 50 | <1 | <5 | <0.2 | <1 | 40 |
| | | | b | 684 | 619 | 3.17 | <0.05 | 1.7 | <0.5 | <0.2 | 27 | 1.6 | 17 | 7.6 | 324 | 46 | <1 | <5 | <0.2 | 1.0 | 56 |
| | 14 | | a | 629 | 848 | 3.31 | <0.01 | 1.3 | <1 | 0.20 | 32 | 2.0 | 18 | 27 | 410 | 64 | <2 | <3 | <0.2 | 7.5 | 74 |
| | | | b | 649 | 939 | 3.25 | <0.01 | 1.5 | <1 | 0.20 | 30 | 2.0 | 18 | 21 | 372 | 62 | <2 | <3 | <0.2 | 2.5 | 68 |
| | 35 | | a | 384 | 234 | 3.80 | <0.01 | 0.48 | 19 | 0.10 | 17 | 4.0 | 6.0 | 65 | 210 | 27 | <2 | <3 | 0.60 | 14 | 39 |
| | | | b | 389 | 351 | 3.85 | <0.01 | 0.46 | 22 | <0.1 | 17 | 5.0 | 6.0 | 73 | 212 | 30 | <2 | <3 | 0.60 | 17 | 42 |
| WL 5.5 | 1 | 5-20 | a | 634 | 708 | 3.37 | <0.02 | 3.1 | 1.4 | 0.81 | 50 | 1.4 | 8.8 | 0.29 | 594 | 99 | 5.2 | <2 | 0.18 | <0.6 | 44 |
| | | | b | 639 | 583 | 3.42 | <0.02 | 2.5 | 0.86 | 0.58 | 44 | 0.99 | 7.5 | 0.25 | 529 | 84 | 3.7 | <2 | 0.14 | <0.6 | 42 |
| | 7 | | a | 719 | 514 | 3.35 | <0.05 | 1.8 | <0.5 | 0.60 | 53 | 1.2 | 9.0 | 0.21 | 596 | 102 | 1.0 | <5 | <0.2 | <1 | 44 |
| | | | b | 729 | 519 | 3.35 | <0.05 | 2.3 | <0.5 | 0.60 | 55 | 1.2 | 11 | 0.27 | 609 | 107 | 2.0 | <5 | <0.2 | <1 | 56 |
| | 14 | | a | 684 | 756 | 3.35 | <0.01 | 2.0 | <1 | 0.80 | 60 | 1.0 | 14 | 1.0 | 674 | 111 | 2.0 | <3 | <0.2 | <0.5 | 86 |
| | | | b | 699 | 769 | 3.35 | <0.01 | 2.3 | <1 | 0.60 | 64 | 1.0 | 16 | 1.1 | 732 | 120 | 4.0 | <3 | <0.2 | <0.5 | 88 |
| | 35 | | a | 594 | 360 | 3.27 | <0.01 | 1.1 | <2 | 0.78 | 58 | 1.4 | 11 | 11 | 590 | 91 | <2 | <10 | 0.47 | 1.8 | 140 |
| | | | b | 599 | 362 | 3.39 | <0.01 | 1.1 | <2 | 0.71 | 52 | 1.3 | 9.6 | 15 | 554 | 87 | <2 | <10 | 0.30 | 1.1 | 139 |

< value is below detection limit

# APPENDIX 3 MONOSULFIDE FORMATION POTENTIAL DATA

## Swanport wetland

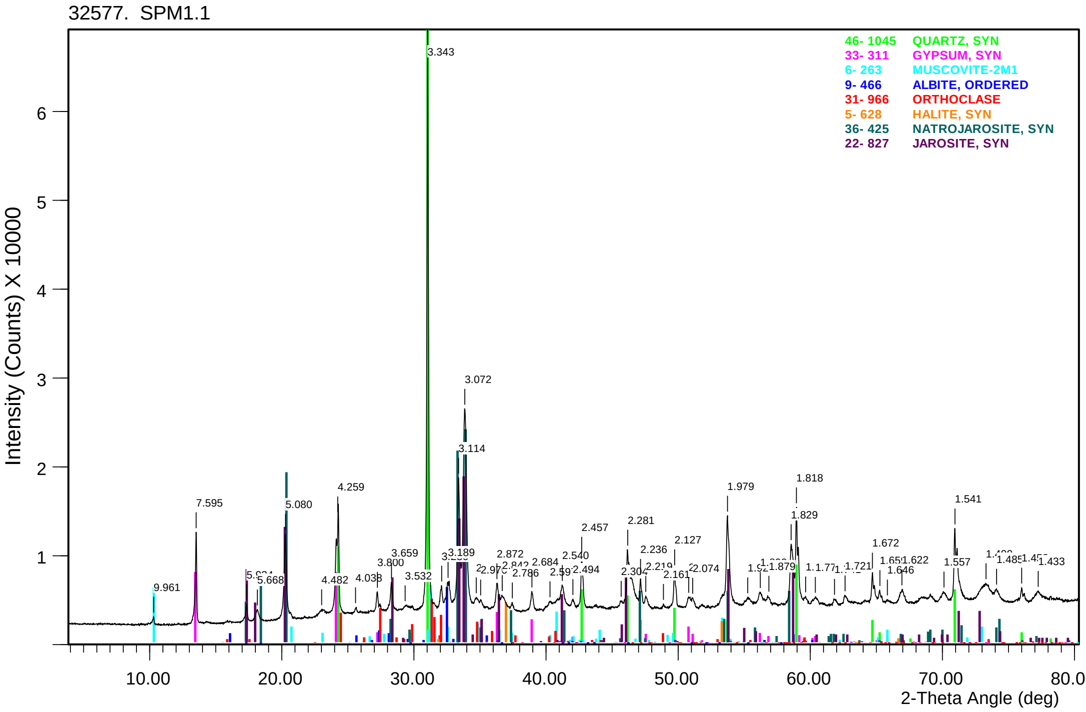
**MBO Formation Potential (MBO FP) - DAY 0** **IRON DATA** **DAY 0**

| | | | | Total Reactive Fe (mg/kg) | | | | Fe(II) (mg/kg) | | | | Eh (mV) | | | | pH | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | org | Site Name | **Site ID** | Replicate 1 | Replicate 2 | **Mean** | +/- | Replicate 1 | Replicate 2 | **Mean** | +/- | Replicate 1 | Replicate 2 | **Mean** | +/- | Replicate 1 | Replicate 2 | **Mean** | +/- |
| 14 | csiro | Swanport | SPM1.2 | 7978 | 10338 | **9158** | *1180* | 2183 | 2372 | **2277** | *95* | 526 | 550 | **538** | *12* | 3.59 | 3.53 | **3.56** | 0.03 |
| 32 | - | Blank | - | 0.3 | 0.1 | **0.2** | *0.1* | <0.1 | <0.1 | **<0.1** | *<0.1* | 183 | 186 | **185** | *2* | 6.17 | 6.10 | **6.14** | 0.04 |

| | | | | **AVS (%S)** | | | | **Pyrite (%S)** | | | | **ES (%S)** | | | | **pH** | | | | **Eh (mV)** | | | | **Aqueous Sulfide (µg/L)** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample No.** | **org** | **Site Name** | **Site ID** | 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** | *+/-* |
| 14 | csiro | Swanport | SPM1.2 | 0.00 | 0.00 | **<0.01** | *<0.01* | 0.01 | 0.04 | **0.03** | *0.01* | 0.00 | 0.00 | **<0.01** | *<0.01* | 4.24 | 3.94 | **4.09** | *0.15* | 276 | 42 | **159** | *117* | 932 | <0.1 | **466** | *466* |
| 32 | csiro | Blank | | | | | | | | | | | | | | 5.45 | 5.42 | **5.44** | *0.02* | 325 | 338 | **331** | *6* | < 0.1 | < 0.1 | < 0.1 | <0.1 |

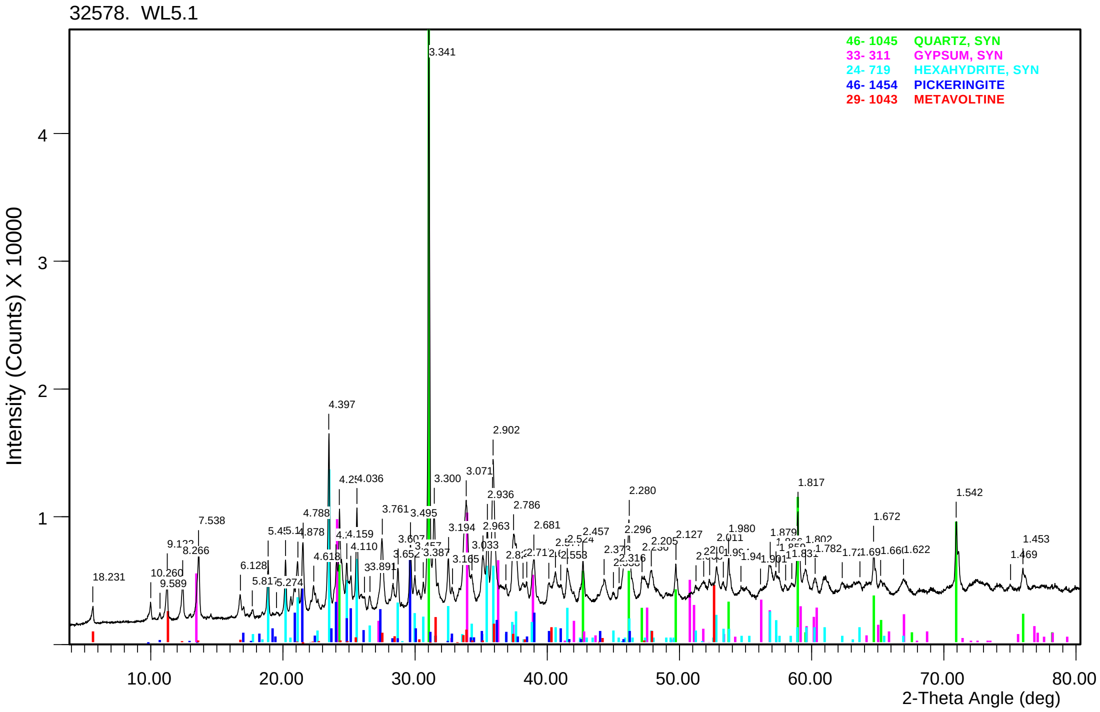
# APPENDIX 4 X-RAY DIFFRACTION DATA

# Sample ID: SPM 1.1



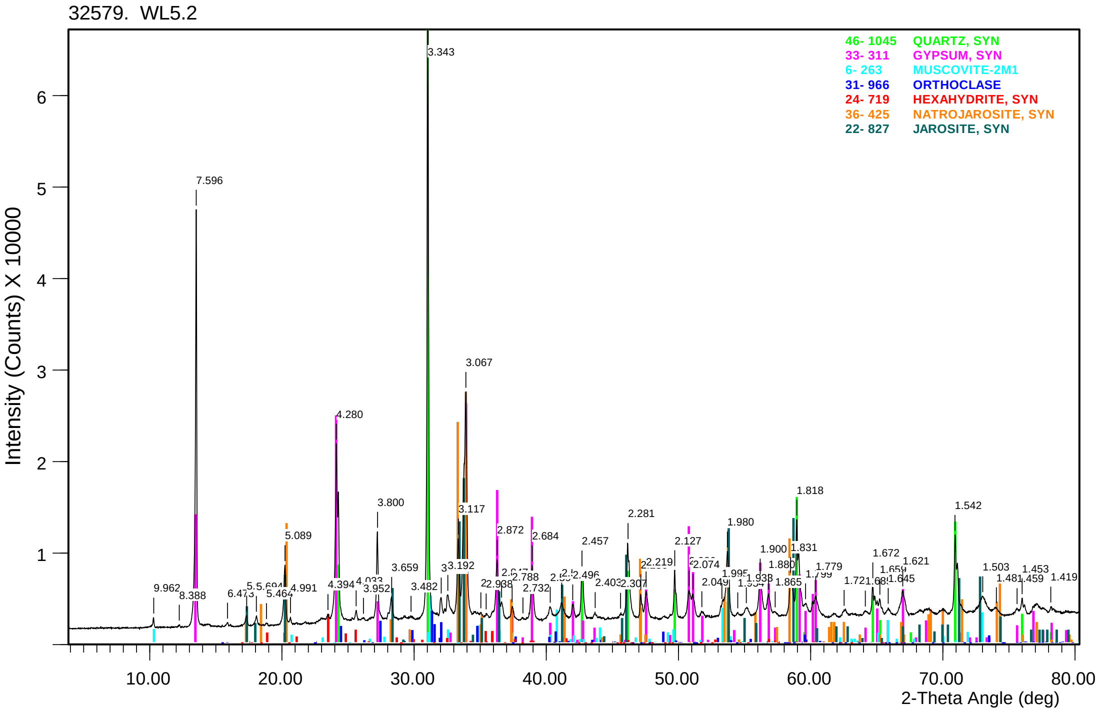
File Name:   c:\...\xpert data\2327_p_shand_salts\32577.xpt

# Sample ID: WL 5.1



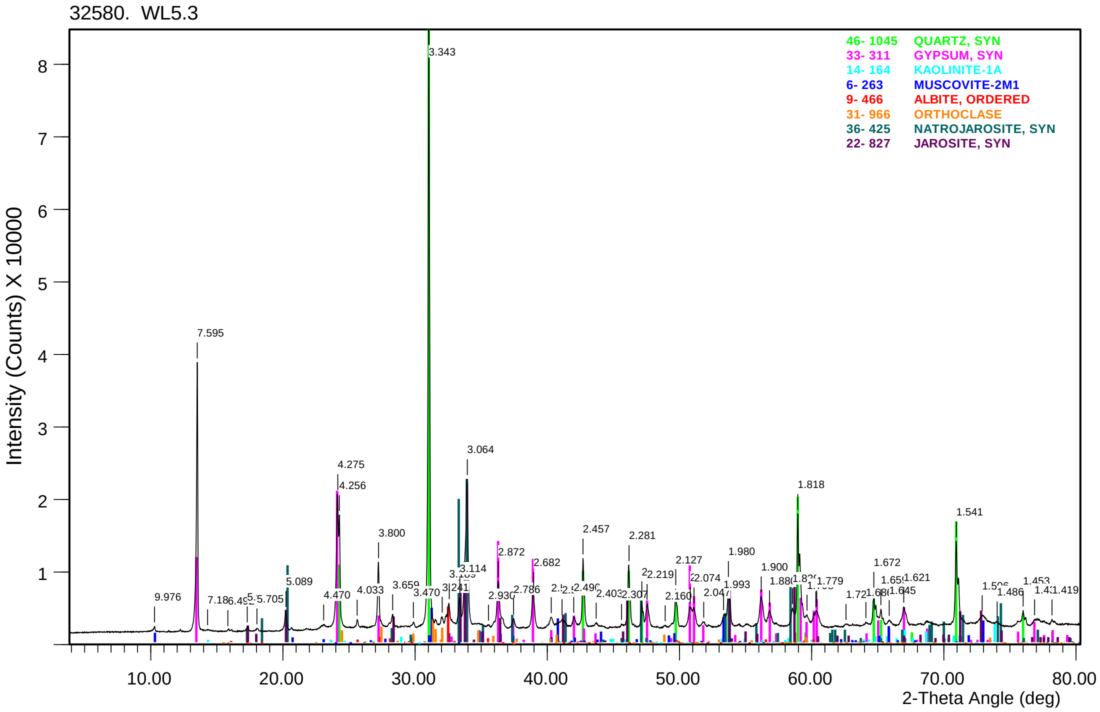
File Name: c:\...\xpert data\2327_p_shand_salts\32578.xpt

# Sample ID: WL 5.2



File Name: c:\...\xpert data\2327_p_shand_salts\32579.xpt

# Sample ID: WL5.3



File Name: c:\...\xpert data\2327_p_shand_salts\32580.xpt

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